

2,3,6,7-Tetramethyl-*cis*-4a,5,8,8a-tetrahydro-1,4-naphthoquinone

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Abstract. C₁₄H₁₈O₂, monoclinic, $P2_1/c$; $a = 5.245$ (2), $b = 29.452$ (7), $c = 8.278$ (5) Å, $\beta = 106.44$ (4)°; $d_m = 1.17$ (flotation), $d_x = 1.182$ g cm⁻³, $Z = 4$; $\mu(\text{Cu } K\alpha) = 6.2$ cm⁻¹. The conformation of the molecule is twisted such that the bridgehead hydrogen atoms are staggered with a torsion angle of 56°. Bond lengths and angles are close to normal values.

Introduction. Small, colourless needles were obtained by slow crystallization from petroleum spirit. Unit-cell and intensity data were measured on a Datex-automated G.E. XRD 6 diffractometer with Cu $K\alpha$ radiation and the θ - 2θ scan technique. Unit-cell parameters were refined by least squares from the observed 2θ values of 19 reflexions. Of the 2442 independent reflexions with $2\theta < 145^\circ$, 1395 had intensities greater than $3\sigma(I)$ above background [$\sigma^2(I) = S + B + (0.04S)^2$, where $S = \text{scan}$ and $B = \text{background count}$]. Lorentz and polarization corrections were applied and the structure amplitudes derived. Crystal dimensions were $0.025 \times 0.010 \times 0.010$ cm and no absorption correction was applied.

The structure was solved by direct methods with the multiresolution procedure (Long, 1965) and observations for which $2\theta < 120^\circ$ only. The best E map clearly showed the positions of all the non-hydrogen atoms. The atoms were refined for several cycles of full-matrix least squares where the function minimized was $\sum w(|F_o| - |F_c|)^2$ with weights $w = 1/\sigma^2(F)$, $\sigma(F)$ values being derived from the previously calculated $\sigma(I)$ values. Twelve of the hydrogen atoms were located on the difference map and the remaining six appeared on a subsequent difference map. Refinement was continued with all non-hydrogen atoms included with anisotropic temperature factors, the hydrogen atoms being refined isotropically, and all 2442 observations. Analysis of the weighting scheme showed ten planes to be in poor agreement. One of these, 040, appeared to be suffering from extinction but the rest seemed to be affected by instrument malfunction. This was confirmed by examination of the preliminary X-ray films and these planes were given zero weight in the final cycles of refinement. The final R and R' $\{ = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} \}$ for the 1395 reflexions with $I > 3\sigma(I)$ are 0.072 and 0.080 respectively. For all 2442 data R is 0.120 and R' is 0.081. The error in an observation of unit weight, $[\sum w(|F_o| - |F_c|)^2 / (m - n)]^{1/2}$, is 1.87. Atomic scattering factors for O and C are those of Cromer & Mann (1968) and for H those of Stewart, Davidson &

Simpson (1965). Final positional and thermal parameters are listed in Tables 1 and 2.*

Thermal-motion analysis and correction of bond lengths for libration were carried out as for 2,3,4a β -5 β ,8 β ,8a β -hexamethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (Phillips & Trotter, 1976b). The r.m.s. ΔU_{ij} for the ten-atom core was 0.0028 Å² and the least-squares r.m.s. $\sigma(U_{ij})$ was 0.0024 Å². Corrected bond lengths are given in Table 3. Bond angles were not significantly affected and corrected values are not reported.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31853 (23 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Final positional parameters (fractional $\times 10^4$, $\text{H} \times 10^3$) with estimated standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
O(1)	4480 (6)	8994 (1)	4052 (4)
O(2)	13177 (6)	8044 (1)	6846 (4)
C(1)	6612 (7)	8799 (1)	4500 (4)
C(2)	6799 (7)	8311 (1)	4072 (5)
C(3)	8917 (8)	8059 (1)	4869 (5)
C(4)	11157 (7)	8257 (1)	6218 (5)
C(5)	10764 (7)	8722 (1)	6846 (5)
C(6)	9413 (9)	8683 (2)	8248 (5)
C(7)	8298 (8)	9117 (1)	8737 (5)
C(8)	7984 (8)	9485 (1)	7778 (5)
C(9)	8705 (10)	9495 (2)	6139 (6)
C(10)	9129 (8)	9035 (1)	5446 (5)
C(11)	4472 (11)	8124 (2)	2727 (8)
C(12)	9198 (15)	7563 (2)	4493 (9)
C(13)	7560 (17)	9086 (3)	10357 (7)
C(14)	6850 (16)	9923 (2)	8228 (9)
H(5)	1234 (7)	886 (1)	727 (4)
H(6a)	1084 (8)	856 (1)	908 (5)
H(6b)	802 (7)	847 (1)	791 (4)
H(9a)	722 (8)	964 (1)	529 (5)
H(9b)	1031 (8)	970 (1)	628 (5)
H(10)	1007 (7)	908 (1)	473 (5)
H(11a)	287 (12)	829 (2)	261 (7)
H(11b)	404 (11)	784 (2)	294 (8)
H(11c)	502 (12)	810 (2)	176 (8)
H(12a)	855 (14)	751 (2)	339 (10)
H(12b)	1104 (14)	747 (2)	477 (8)
H(12c)	832 (17)	740 (3)	518 (12)
H(13a)	918 (13)	900 (2)	1105 (8)
H(13b)	644 (18)	928 (3)	1057 (11)
H(13c)	631 (15)	883 (2)	1042 (9)
H(14a)	500 (13)	996 (2)	765 (8)
H(14b)	759 (14)	1015 (3)	764 (11)
H(14c)	748 (14)	1000 (2)	920 (8)

Table 2. Final thermal parameters and their estimated standard deviations

Anisotropic thermal parameters in the expression:

$$f = f^0 \exp [-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)].$$

(a) Anisotropic thermal parameters ($U_{ij} \times 10^3 \text{ \AA}^2$)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	48 (2)	82 (2)	67 (2)	14 (2)	5 (1)	9 (2)
O(2)	54 (2)	74 (2)	89 (2)	19 (2)	1 (2)	7 (2)
C(1)	41 (2)	70 (3)	31 (2)	3 (2)	11 (2)	16 (2)
C(2)	44 (2)	64 (3)	37 (2)	-5 (2)	13 (2)	3 (2)
C(3)	55 (2)	56 (3)	48 (2)	-3 (2)	19 (2)	1 (2)
C(4)	46 (2)	57 (3)	51 (2)	6 (2)	15 (2)	9 (2)
C(5)	33 (2)	58 (3)	45 (2)	-2 (2)	3 (2)	5 (2)
C(6)	55 (3)	57 (3)	36 (2)	0 (2)	5 (2)	7 (2)
C(7)	51 (2)	58 (3)	40 (2)	1 (2)	8 (2)	-1 (2)
C(8)	51 (2)	52 (3)	47 (2)	0 (2)	8 (2)	-4 (2)
C(9)	63 (3)	56 (3)	52 (3)	-7 (2)	13 (2)	14 (2)
C(10)	46 (2)	56 (3)	40 (2)	1 (2)	18 (2)	12 (2)
C(11)	58 (3)	85 (4)	63 (3)	-9 (3)	5 (3)	-8 (3)
C(12)	90 (4)	67 (4)	71 (4)	6 (3)	14 (3)	-6 (3)
C(13)	104 (5)	107 (5)	44 (3)	8 (4)	36 (3)	6 (3)
C(14)	99 (5)	70 (4)	70 (4)	16 (3)	8 (4)	-6 (3)

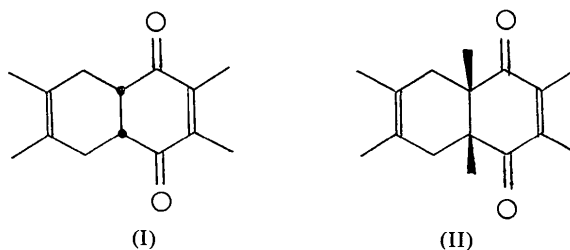
(b) Isotropic thermal parameters ($U_{iso} \times 10^2 \text{ \AA}^2$)

	U		U		U
H(5)	4 (1)	H(11a)	12 (2)	H(13a)	13 (2)
H(6a)	6 (1)	H(11b)	13 (3)	H(13b)	21 (4)
H(6b)	5 (1)	H(11c)	14 (3)	H(13c)	17 (3)
H(9a)	7 (1)	H(12a)	17 (3)	H(14a)	12 (2)
H(9b)	7 (1)	H(12b)	14 (3)	H(14b)	18 (4)
H(10)	5 (1)	H(12c)	23 (5)	H(14c)	15 (3)

Table 3. Bond lengths (\AA) for non-hydrogen atoms with estimated standard deviations in parentheses

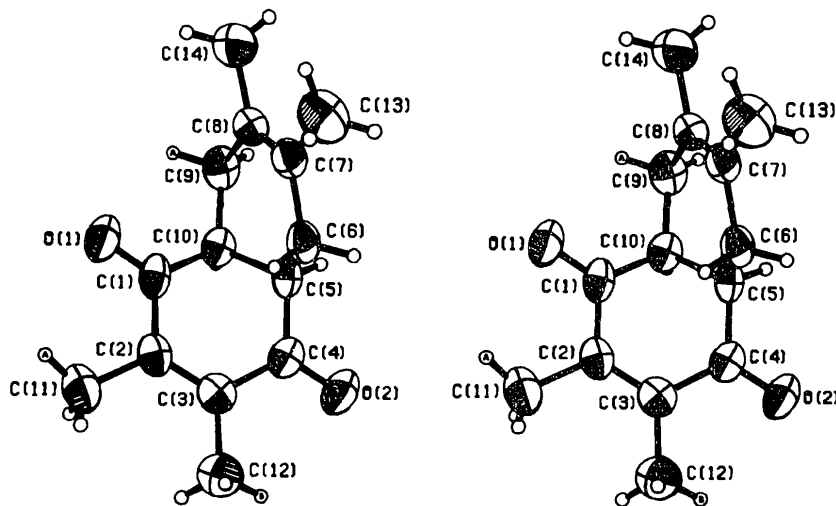
	Corrected		Corrected
O(1)-C(1)	1.217 (4)	O(2)-C(4)	1.215 (4)
C(1)-C(2)	1.491 (6)	C(1)-C(10)	1.501 (5)
C(2)-C(3)	1.344 (5)	C(3)-C(4)	1.492 (5)
C(4)-C(5)	1.500 (6)	C(5)-C(6)	1.526 (5)
C(5)-C(10)	1.537 (5)	C(6)-C(7)	1.509 (6)
C(7)-C(8)	1.326 (5)	C(8)-C(9)	1.508 (6)
C(9)-C(10)	1.514 (6)	C(2)-C(11)	1.505 (6)
C(3)-C(12)	1.510 (7)	C(7)-C(13)	1.500 (6)
C(8)-C(14)	1.509 (7)		1.502

Discussion. The structural work on 2,3,6,7-tetramethyl-*cis*-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (I) was undertaken as part of a study of the photochemistry of various substituted 1,4-naphthoquinone systems with *cis* bridgehead substituents.



A stereo diagram of the molecule, with the crystallographic numbering scheme, is shown in Fig. 1. The conformation is staggered about the C(5)-C(10) bond as in *cis*-2,3,4a,6,7,8a-hexamethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (II) (Phillips & Trotter, 1976a). The torsion angles C(6)-C(5)-C(10)-C(1) and H(5)-C(5)-C(10)-H(10) are -71.4 (4) and 56 (3) $^\circ$ respectively, compared to corresponding values in (II) of -61.4 (5) and 60.0 (6) $^\circ$. The decrease in 'twist' about the central C(5)-C(10) bond as compared with (II) is due to the reduction in steric hindrance effected by replacing the bulky methyl groups at the bridgehead positions by hydrogen atoms.

This conformational change produces a slight reduction in the distance between the carbonyl oxygen O(1) and the β -hydrogen H(9a) from 2.47 (6) \AA in (II) to 2.42 (6) \AA in (I). A further consequence is an increase in the distance of H(6b) from the C(2)=C(3) double bond, H(6b) \cdots C(2) being 3.09 (6) and H(6b) \cdots C(3) 2.94 (6) \AA , a change from the corresponding values in (II) of 0.20 and 0.14 \AA respectively. The expected effect on the photochemistry of (I) would be to favour the β -hydrogen abstraction pathway over abstraction

Fig. 1. Stereo diagram of 2,3,6,7-tetramethyl-*cis*-4a,5,8,8a-tetrahydro-1,4-naphthoquinone.

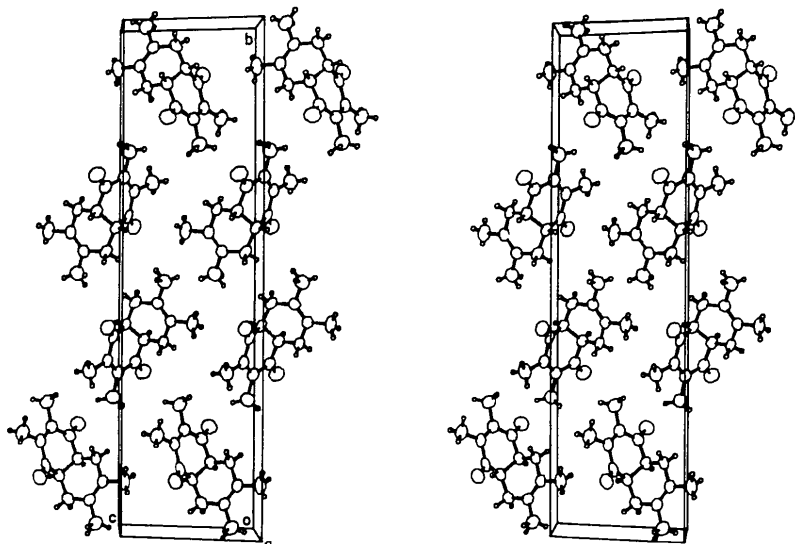


Fig. 2. Stereo diagram of the contents of the unit cell projected down the *a* axis.

Table 4. Bond angles ($^{\circ}$) for non-hydrogen atoms with estimated standard deviations in parentheses

O(1)—C(1)—C(2)	119.9 (4)	O(1)—C(1)—C(10)	122.5 (4)
C(2)—C(1)—C(10)	117.5 (3)	C(1)—C(2)—C(3)	121.1 (4)
C(2)—C(3)—C(4)	121.1 (4)	O(2)—C(4)—C(3)	121.5 (4)
O(2)—C(4)—C(5)	120.9 (4)	C(3)—C(4)—C(5)	117.4 (3)
C(4)—C(5)—C(6)	109.5 (4)	C(4)—C(5)—C(10)	112.8 (3)
C(6)—C(5)—C(10)	109.8 (3)	C(5)—C(6)—C(7)	116.0 (4)
C(6)—C(7)—C(8)	121.6 (4)	C(7)—C(8)—C(9)	122.3 (4)
C(8)—C(9)—C(10)	115.1 (4)	C(1)—C(10)—C(5)	109.7 (3)
C(1)—C(10)—C(9)	114.2 (4)	C(5)—C(10)—C(9)	111.2 (3)
C(1)—C(2)—C(11)	115.8 (4)	C(3)—C(2)—C(11)	123.1 (4)
C(2)—C(3)—C(12)	123.3 (4)	C(4)—C(3)—C(12)	115.6 (4)
C(6)—C(7)—C(13)	113.9 (4)	C(8)—C(7)—C(13)	124.4 (5)
C(7)—C(8)—C(14)	122.7 (5)	C(9)—C(8)—C(14)	115.0 (4)

by enone carbon. The observed solution photochemistry of (I) (Scheffer, Bhandari, Gayler & Wostradowski, 1975) shows that the pathway followed is exclusively β -hydrogen abstraction. Irradiation of crystals of (I), however, appears to give no reaction (Scheffer & Dzakpasu, 1975) whereas (II) behaves in a similar fashion whether in solution or the solid state. The only significant intermolecular contact to O(1), the O atom that abstracts the β -hydrogen, involves the O(2)=C(4) carbonyl group of a neighbouring molecule. The distance O(1)···C(4) [$1+x,y,z$] is 3.567 Å and O(1)···

O(2) [$1+x,y,z$] is 3.813 Å. The mean planes of the two carbonyl groups subtend an angle of 16.42°. Other intermolecular contacts correspond to van der Waals interactions. A packing diagram of the structure is shown in Fig. 2. Bond lengths and angles are given in Tables 3 and 4.

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References

- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A24, 321–324.
- LONG, R. E. (1965). Ph. D. Thesis, Univ. of California.
- PHILLIPS, S. E. V. & TROTTER, J. (1976a). *Acta Cryst.* B32, 3088–3091.
- PHILLIPS, S. E. V. & TROTTER, J. (1976b). *Acta Cryst.* B32, 3091–3094.
- SCHEFFER, J. R., BHANDARI, K. S., GAYLER, R. E. & WOSTRADOWSKI, R. A. (1975). *J. Amer. Chem. Soc.* 97, 2178–2189.
- SCHEFFER, J. R. & DZAKPASU, A. A. (1975). Unpublished results.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175–3187.